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Vibrational Anisotropy from Single-crystal NRVS of [Fe(OEP)(NO)]

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Nuclear resonance vibrational spectroscopy (NRVS) on single crystals of [Fe(Por)(L)] has traditionally been done with the incident x-ray beam either perpendicular or parallel to the mean porphyrin plane. Iron out-of-plane modes are observed when perpendicular and iron in-plane modes when parallel. Previously, the parallel orientation was made without specifying a radial angle, so any inherent directional dependence of in-plane mode intensities could not be observed. We conducted NRVS on single crystals of [Fe(OEP)(NO)] oriented so that spectra along any in-plane direction were achievable. In-plane anisotropy was found to be axial-ligand directed with the iron motion of nearly all modes parallel or perpendicular to the Fe-NO plane. Comparisons to density functional theory-predicted spectra allow for mode assignments and demonstrate the sensitivity of NRVS to very small iron displacement. Vibrational modes can now be more accurately categorized as purely in plane, purely out of plane or an admixture of the two. This more exhaustive characterization of vibrational modes may be useful in the elucidation of the heme-NO binding associated with biological signaling.